

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Recovery of Krypton and Xenon from Air

We, THE BRITISH OXYGEN COMPANY LIMITED, a British Company, of Bridgewater House, Cleveland Row, St. James's, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the recovery of krypton and xenon and more particularly to their recovery from the atmosphere during the low temperature separation of atmospheric air.

The concentrations of krypton and xenon in the atmosphere are very small, being approximately 1.1 and 0.09 volumes per million respectively. The boiling points of krypton (-153°C.) and xenon (-108°C.) are appreciably above those of oxygen (-183°C.) and nitrogen (-196°C.), and in the course of the low temperature separation of air by liquefaction and rectification, these rare gases are concentrated in the liquid oxygen bath at the base of the final rectification column.

Since only small quantities of krypton and xenon escape with the nitrogen product, for steady state operation of an air separation plant, almost the whole of the krypton and xenon in the inlet air are withdrawn in the oxygen product, which may be either in the liquid or the gaseous state. Since the oxygen product is usually of the order of one-fifth of the total air processed, the krypton and xenon are therefore usually concentrated some five times in the oxygen product. The concentrations are, however, still very small, about 0.45 and 5.5 volumes per million for xenon and krypton respectively.

Hitherto, these rare gases have usually been recovered by subjecting the oxygen product to a further rectification in an additional column to produce a fraction in which the krypton and xenon are further concentrated, and removing the oxygen from this fraction by chemical methods, such as combustion with hydrogen. This is a complicated procedure, involving the

provision of additional equipment. It has also been proposed to remove oxygen from admixture with the rare gases by the use of absorbents for the oxygen, for example, charcoal.

It is an object of the present invention to provide a method of recovering krypton and xenon in the low temperature separation of air which is simple to operate and does not require the provision of expensive equipment.

According to one aspect of the present invention, a process for the recovery of krypton and xenon from air comprises separating the air into a nitrogen fraction and an oxygen fraction, passing the oxygen fraction at a temperature substantially below atmospheric temperature and preferably not substantially above its boiling point through an adsorbent bed of a zeolite of the molecular sieve type, as hereinafter defined, having a pore size such that the krypton and xenon are preferentially adsorbed, and subsequently heating the zeolite to desorb the krypton and xenon therefrom.

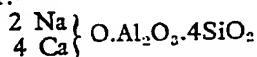
According to another aspect of the present invention, a process for the recovery of krypton and xenon comprises passing an oxygen fraction derived from the low temperature separation of air at a temperature substantially below atmospheric temperature and preferably not substantially above its boiling point, through an adsorbent bed of a zeolite of the molecular sieve type, as hereinafter defined, having a pore size such that the krypton and xenon are preferentially adsorbed, and subsequently heating the zeolite to desorb the krypton and xenon therefrom.

The zeolites which are to be used as molecular sieves may be naturally occurring or synthetic materials. They are crystalline aluminosilicates, which normally contain a high proportion of water of crystallisation which occupies sites within the crystal lattice. When heated under vacuum, zeolites of the molecular sieve type give up their water of crystallisation, but owing to their strong 3-dimensional cross-linking, the crystal lattice is maintained to

[Price 3s. 6d.]

almost complete dehydration without collapse. The resultant porous structure containing the sites vacated by water molecules has the property of accommodating molecules of sufficiently small diameter inside its crystal lattice, exhibiting very high sorptive capacities even at low partial pressures.

A zeolite which is particularly suitable for the recovery of krypton and xenon is a synthetic sodium calcium aluminosilicate having the formula:—



and having a pore size of approximately 5 Å. Another zeolite, particularly suitable for the recovery of krypton and xenon is a synthetic material having the formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ and a pore size of approximately 13 Å. Any other zeolite of the molecular sieve type having suitable sorption characteristics may, however, be used.

One method of carrying out the process of the present invention is illustrated in the accompanying drawing, which shows diagrammatically apparatus for carrying out the process attached to a conventional double-column air separation plant producing liquid oxygen. In the drawing, only the double column of such a plant is shown, the remaining parts of the plant, such as the air compression and heat exchange systems, which are well known to those skilled in the art being omitted.

Referring to the drawing, the double column R functions in known manner, air at a pressure of approximately 5.6 atmospheres absolute and a temperature of 98° K. being fed to the lower column and gaseous nitrogen and liquid oxygen being withdrawn from the upper column at a pressure normally a few pounds per square inch above atmosphere. The gaseous nitrogen is substantially free from krypton and xenon, which are substantially all contained in the liquid oxygen fraction. This fraction is withdrawn through a pipe 10 and passed through one of a pair of alternating adsorbers Z₁ and Z₂ which contain a suitable molecular sieve. During such passage, the krypton and xenon are adsorbed. The liquid oxygen leaving the adsorber is passed to storage. Alternation of the adsorbers is effected by the manipulation of change-over valves, V₁, V₂, V₃, V₄, V₅ and V₆. For example, if the active adsorber is Z₁, valves V₂, V₃, V₄ will be open and valves V₁, V₅ and V₆ closed. When the zeolite in the adsorber Z₁ is saturated with the adsorbate, the liquid oxygen is diverted to adsorber Z₂ by closing valves V₂, V₃ and V₄ and opening valves V₁ and V₆. The adsorber Z₁ is meanwhile drained by opening drain valve D₁ until it is free from liquid oxygen and valve V₁ is then opened and the adsorber Z₁ allowed to warm up to ambient temperature. During this phase, the adsorbed rare gas is desorbed together with some adsorbed oxygen and is collected through line 12. It is

advantageous towards the end of the warming up process to evacuate the adsorber in order to effect complete removal of the adsorbed gas. The desorbed mixture may be further purified, if desired, to recover the rare gas as a relatively pure product.

In a particular example, using a zeolite of pore size approximately 5 Å, liquid oxygen leaving the double column contained 0.4 parts per million of xenon (expressed as the volume of xenon at ambient temperature and pressure in a million volumes of liquid oxygen measured under the same conditions). The liquid oxygen was passed through a bed of the zeolite. It was found that when saturated, the zeolite had adsorbed some 0.02 c.c./gm. of xenon, corresponding to approximately 10 c.c. (free gas) of xenon per pound of adsorbent. Krypton present in the liquid oxygen was also adsorbed by the zeolite.

Where the oxygen is produced in the gaseous state, the adsorbers may be simply inserted in the gaseous oxygen offtake from the air separation plant. Alternatively, liquid oxygen from the condenser of the column may be circulated through the adsorber and thereafter fed back to the condenser.

To illustrate the efficiency of xenon removal from gaseous oxygen by a zeolite of pore size approximately 5 Å, liquid oxygen containing 0.4 parts per million of xenon was completely vaporised and the vaporised gas passed through a bed of the zeolite at a temperature of 90° K. and a space velocity not exceeding 5000 hrs⁻¹. Some 40% of the total xenon originally present in the liquid oxygen was adsorbed and subsequently recovered by warming up the adsorbent bed, together with some desorbed oxygen and the krypton present in the vaporised gas.

WHAT WE CLAIM IS:—

1. Process for the recovery of krypton and xenon from air which comprises separating the air into a nitrogen fraction and an oxygen fraction, passing the oxygen fraction at a temperature substantially below atmospheric temperature through an adsorbent bed of a zeolite of the molecular sieve type, as hereinbefore defined, having a pore size such that the krypton and xenon are preferentially adsorbed, and subsequently heating the zeolite to desorb the krypton and xenon therefrom.

2. Process for the recovery of krypton and xenon which comprises passing an oxygen fraction, derived from the low temperature separation of air, at a temperature substantially below atmospheric temperature through an adsorbent bed of a zeolite of the molecular sieve type, as hereinbefore defined, having a pore size such that the krypton and xenon are preferentially adsorbed, and subsequently heating the zeolite to desorb the krypton and xenon therefrom.

3. Process according to Claim 1 or Claim 2 wherein said oxygen fraction is at a tempera-

ture not substantially above its boiling point.

4. Process according to any of the preceding claims wherein said zeolite has a pore size of approximately 5 Å.

5. Process according to any of Claims 1 to 3 wherein said zeolite has a pore size of approximately 13 Å.

6. Process for the recovery of krypton and/or xenon from air substantially as hereinbefore described with reference to the accompanying drawing. 10

P. L. SPENCER,
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PROVISIONAL SPECIFICATION

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Since only small quantities of krypton and xenon escape with the nitrogen product, for steady state operation of an air separation plant, almost the whole of the krypton and xenon in the inlet air are withdrawn in the oxygen product, which may be either in the liquid or the gaseous state. Since the oxygen product is usually of the order of one-fifth of the total air processed, the krypton and xenon are therefore concentrated some five times in the oxygen product. The concentrations are, however, still very small, about 0.45 and 5.5 volumes per million for xenon and krypton respectively.

Hitherto, these rare gases have been recovered by subjecting the oxygen product to a further rectification in an additional column to produce a fraction in which the krypton and xenon are further concentrated, and removing the oxygen from this fraction by chemical methods, such as combustion with hydrogen. This is a complicated procedure, involving the provision of additional equipment.

It is an object of the present invention to provide a method of recovering krypton and xenon in the low temperature separation of air which is simple to operate and does not require the provision of expensive equipment.

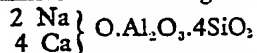
According to one aspect of the present invention, a process for the recovery of krypton and xenon from air comprises separating the air into a nitrogen fraction and an oxygen

fraction, passing the oxygen fraction at a low temperature, preferably of the order of -180°C. through a vessel containing a zeolite of the molecular sieve type, as hereinafter defined, having a pore size such that the krypton and xenon are preferentially adsorbed, and subsequently heating the zeolite to desorb the krypton and xenon therefrom.

According to another aspect of the present invention, a process for the recovery of krypton and xenon comprises passing an oxygen fraction derived from the low temperature separation of air at a low temperature, preferably of the order of -180°C. through a vessel containing a zeolite of the molecular sieve type, as hereinafter defined, having a pore size such that the krypton and xenon are preferentially adsorbed, and subsequently heating the zeolite to desorb the krypton and xenon therefrom.

The zeolites which are to be used as molecular sieves may be naturally occurring or synthetic materials. They are crystalline aluminosilicates, which normally contain a high proportion of water of crystallisation which occupies sites within the crystal lattice. When heated under vacuum, zeolites of the molecular sieve type give up their water of crystallisation, but, owing to their strong 3-dimensional cross-linking, the crystal lattice is maintained to almost complete dehydration without collapse. The resultant porous structure containing the sites vacated by water molecules has the property of accommodating molecules of sufficiently small diameter inside its crystal lattice, exhibiting very high sorptive capacities even at low partial pressures.

A preferred zeolite is a synthetic sodium calcium aluminosilicate having the formula:—



and having a pore size of approximately 5 Å, but other zeolites of the molecular sieve type having suitable sorption characteristics may be used.

The recovery of krypton and xenon by the method of the present invention can conveniently be carried out by inserting the adsorbent in a suitable vessel in the liquid oxygen take-off line from an air separation plant producing the oxygen product as liquid. Preferably, two vessels containing adsorbent are connected in parallel so that one may be in use while the sorbed krypton and xenon are being

recovered from the other. When the adsorbent bed is saturated, it is heated to desorb a mixture of krypton, xenon and oxygen, the rare gases being present in quite high concentration. 10
5 After such treatment the adsorbent is ready for re-use. The desorbed gases can subsequently be purified from oxygen by normal chemical methods or other suitable means. 15
Where the oxygen product is produced in

the gaseous phase, the adsorbent vessels may similarly be inserted in the gaseous oxygen offtake from the plant. Alternatively, liquid oxygen from the condenser of the fractionating column may be circulated through the adsorbent and thereafter fed back into the condenser.

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1 SHEET

COMPLETE SPECIFICATION

This drawing is a reproduction of
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